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A-830

April 20, 1966

Mr. C. H. Bronson, Manager
Sales & Development
Industrial Chemicals
Southwest Potash Corporation
1270 Avenue of the Americas
New York 20, New York

Subject: Final Report, Project A-830, "Laboratory Investigation of Chlorine Produced by a Unique Process."

Dear Mr. Bronson:

The subject report is submitted herewith, and we trust is satisfactory. The time period for this investigation extended far beyond that anticipated due primarily to the desirability of ascertaining the cause of some of the peculiarities in the properties of the alkaline solutions of your gas samples.

While the report is complete in itself, the major conclusions from the work can be stated briefly:

1. Bactericidal properties of the SWP materials were equal or somewhat superior to those of electrolytic chlorine solutions, based upon tests with E-Coli. We can not give a valid explanation of this.

2. Against the influence of ultraviolet, SWP chlorine solutions had a storage stability essentially equal to that of electrolytic chlorine solutions.

3. It was determined that NaCl and $NaNO_3$ formed in the SWP solutions. The presence of $NaNO_3$, which is an algal nutrient, makes SWP solutions undesirable for certain sanitary chemical uses such as a swimming pool disinfectant. For other uses, such as "one-time" applications, the $NaNO_3$ would have no deleterious effect.

4. Corrosion of the steel gas cylinder was noted, due probably to a reaction between trace quantities of water and nitrogen oxides. Apparently, $NaNO_2$, which is a corrosion inhibitor, is formed only as an intermediate compound and is oxidized; thus its inhibitive properties are lost.

If you have any questions concerning the data or conclusions, please let me know and I will try to answer them.

Very truly yours,

R. S. Ingols
Project Director

RSI:lg
Addressee in duplicate

FINAL REPORT

PROJECT A-830

LABORATORY EVALUATION OF CHLORINE PRODUCED BY A UNIQUE PROCESS

Prepared for

SOUTHWEST POTASH CORPORATION

By

Robert S. Ingols
J. E. McCallum

April 1966

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY
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LABORATORY EVALUATION OF CHLORINE PRODUCED BY A UNIQUE PROCESS

INTRODUCTION

The Southwest Potash Corporation (SWP) produces chlorine by a chemical process. A gas mixture roughly 98 percent chlorine and 2 percent nitrogen oxides (calculated as NOCl) is available. When this gas is dissolved to form a "bleach" solution, it was considered possible that the presence of the nitrogen oxides might impart better storage stability, decrease corrosion of equipment, and still be as good a bleach-disinfectant as solutions produced from conventional electrolytic chlorine.

Accordingly, this Project was initiated in January 1965.

EXPERIMENTAL

Two samples of solutions in plastic containers were received from SWP, and designated as SWP1 and SWP2, and were so identified throughout the investigation. It was understood that these samples were prepared by dissolving a chlorine-nitrogen oxides gas, roughly 98 percent and 2 percent respectively, in an NaOH solution.

Two samples of SWP gas mixture in steel bombs also were received. Corrosion, however, with resultant gas composition and pressure changes, was so severe that no work was carried out on these samples.

Analyses of Solutions

Throughout the test period, both SWP samples had a pH of 11.0 or higher, showing a considerable excess of alkali not normally encountered in commercial hypochlorite solutions.

Residual chlorine normalities were markedly different in the two samples as shown by the following.

Sample	SWP1	SWP2
Normality of chloride ion at start of investigation	0.409	1.580
Actual chloride ion normality after reduction with Na_2SO_3	1.806	3.921
Theoretical chloride ion normality after complete reduction	0.818	3.160

This discrepancy, and differences (noted later) in ultraviolet stability and bactericidal action when compared with electrolytic chlorine alkali solutions, pointed to the need for definite characterization of the components in the SWP solutions in order to understand the results. Actually it was not until near the end of the investigation that a plausible sequence of reactions in the SWP solutions to form $NaNO_3$ and NaCl was confirmed. Without this knowledge, results being obtained were inexplicable, and caused considerable delays in project work as it was not thought advisable to proceed without a firm foundation to plan further tests.

It seemed obvious that some active group other than hypochlorite ion was present, and $NaNO_2$, $NaNO_3$ and NaCl seemed to be likely candidates for being formed. A Beckman DK-2 spectrophotometer offered a simple, direct, quick technique for investigation. After some trial-and-error, it was found that the transmission curve, over the range from 220 to 340 millimicrons wave length, for SWP2, could be duplicated almost perfectly simply by adding certain amounts of NaCl and $NaNO_3$ to an electrolytic chlorine solution.

The maximum deviation was but 1 percent over the range of about 270 to 320 millimicrons; the curves being practically identical for the other ranges. Both the SWP2 and the electrolytic chlorine solution were diluted 1:1000 with distilled water, and run at a pH of 9.6. The concentrations of NaCl and $NaNO_3$, added to the electrolytic chlorine solution, were 0.082 and 0.0120 grams per liter respectively.

Accordingly, it was calculated that the SWP2 solution contained 38 grams NaOCl per liter, 140 grams NaCl per liter and 12 grams $NaNO_3$ per liter. The large concentration of NaCl is in part a result of a slow decomposition of hypochlorite, and in a smaller part, a result of the reduction of chlorine consumed by oxidation of nitrous acid to the nitrate.

The mechanism leading to the formation of NaCl and $NaNO_3$ in the SWP solutions can be understood by the following series of plausible reactions.

$$Cl_2 + H_2O = HCl + HOCl \quad (1a)$$

$$Cl_2 + 2NaOH = NaCl + NaOCl + H_2O \quad (1b)$$

$$HCl + NaOH = NaCl + H_2O \quad (2a)$$

$$2NaOCl + N_2O + H_2O = 2NOCl + 2NaOH \quad (2b)^*$$

$$NOCl + H_2O = HCl + HNO_2 \quad (3a)$$

$$NOCl + 2NaOH = NaCl + NaNO_2 + H_2O \quad (3b)$$

$$NaOCl + NaNO_2 = NaCl + NaNO_3 \quad (4a)$$

$$HOCl + HNO_2 = HCl + HNO_3 \quad (4b)$$

$$HNO_3 + NaOH = NaNO_3 + H_2O \quad (5)$$

The overall reaction is:

$$4Cl_2 + 10NaOH + N_2O = 2NaNO_3 + 8NaCl + 5H_2O$$

*Presence of N_2O seems unlikely. It was not known if NOCl was in the "nitrogen oxide gases" or if, in solution, $2NO + Cl_2 = 2NOCl$. In NaOH solutions, part of NO reacts to form N_2O and $NaNO_2$, the bulk of NO forming $NaNO_3$ with evolution of N_2.

Bactericidal Properties

A solution containing E-Coli and 50 milligrams per liter of Peptone was treated with the bleach solutions in such amount as to give varying amounts of chlorine in the combined solutions. After fifteen minutes a count of the viable organisms remaining provided a measure of the bactericidal power of the solutions. The data are given in Table I. The first set of data was obtained early in the project and indicated that the SWP solutions were somewhat superior in bactericidal action. The effectiveness in SWP2 seemed to increase with titratable chlorine, while in SWP1 was independent of the chlorine concentration over the range between 0.05 and 0.50 ppm.

As a means of understanding the better bactericidal properties of the SWP solutions, an attempt was made to determine a "point of attack" on component residues of a protein molecule (Peptone). Acid-base titrations on SWP1 and a commercial bleach solution against oxalic acid, glutamic acid, cystine, tyrosine and methionine offered a method of sequentially examining differences in the effect of the chlorine solutions on the carboxyl, amine, disulphide, tyrosine and thioether functional groups of the protein molecule. No significant differences were found.

The second set of data in Table I was obtained within two weeks of the first set. Surprisingly, there were no significant differences between the solutions. It is apparent that the second run was made on an E-Coli solution much less concentrated than the first, but no logical reason can be offered to explain the different behavior.

TABLE I

EFFECT OF CHLORINE SOLUTIONS ON E-COLI

RUN 1

Chlorine, ppm	VIABLE ORGANISMS PER MICROLITER AFTER 15 MIN.	
	Electrolytic	SWP1
0.00	241	241
0.05	194	51
0.10	203	49
0.15	188	53
0.20	223	23
0.25	162	22
0.30	174	28
0.35	176	39
0.40	200	33
0.45	209	27
0.50	211	0

RUN 2

Chlorine, ppm	VIABLE ORGANISMS PER MICROLITER AFTER 15 MIN.		
	Electrolytic	SWP1	SWP2
0.05	21	--	10
0.10	23	15	13
0.15	13	14	10
0.20	16	17	18
0.25	15	19	17
0.30	17	14	25
0.35	15	7	14
0.40	12	15	11
0.45	19	7	10
0.50	--	14	5

Formation of $NaNO_3$ in the SWP solutions will preclude their use for certain sanitary applications, such as swimming pools. Sodium nitrate is an algal nutrient, and would enhance undesirable growth of algae.

Confirmation of this mechanism was checked by mixing stoichiometric quantities of $NaNO_2$ and NaOCl, and a quantitative yield of chloride ion, per Equation (4a), was obtained.

These reactions also permit an explanation of the higher chloride ion and lower hypochlorite concentration in SWP1 as compared to SWP2. Relatively more of the nitrogen oxide gases must have been absorbed in SWP1 resulting in lower hypochlorites and higher NaCl formation.

Both SWP solutions and a commercial bleach solution were titrated at a pH of 6.4 with neutral orthotolidine. Only chlorine residuals, with no evidence of chloramine compounds, were found.

Stability

Samples of the bleach solutions were exposed to ultraviolet light and the concentration of active chlorine determined by thiosulphate titration of aliquots at 10 minute intervals over a one-hour exposure period.

The chlorine concentration in a commercial bleach solution was almost double that of the SWP1 solution at the beginning of the exposure period. At the end of the one-hour period, both commercial and SWP solutions had lost practically all active chlorine. When adjusted for the difference in initial concentration, the data indicate the two solutions to exhibit essentially equal "Storage Stability" when exposed to light.

Corrosion

The condition of the steel gas cylinders, as noted above, indicates that supply of gas in steel cylinders will be impracticable.

It was hoped that nitrites might be formed from the nitrogen oxide gases and nitrites are known to be effective in inhibiting corrosion of steel. The series of equations, shown above, indicate that any nitrites so formed are oxidized to nitrates and inhibiting effects would not be realized.

Accordingly, corrosion problems seem to be inherent in the manufacture of SWP solutions.

SUMMARY - CONCLUSIONS

1. SWP bleach solutions were found to be quite similar to commercial bleach solutions as regards storage stability and bactericidal effectiveness.

2. SWP solutions were found to contain sodium chloride and sodium nitrate, probably as a result of a series of reactions as outlined herein.

3. Presence of sodium nitrate, a known algal nutrient, would restrict use of SWP solutions where algae are a consideration.

4. Reduction in corrosive action by SWP gases-solutions on steel, in comparison with usual commercial solutions, apparently was not realized.